A study of the microstructure of mechanically alloyed FCC-Fe$_{50}$Cu$_{50}$

LETTER TO THE EDITOR

A study of the microstructure of mechanically alloyed FCC-Fe$_{50}$Cu$_{50}$

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Abstract. The microstructure of the unstable FCC-Fe$_{50}$Cu$_{50}$ alloy prepared by mechanical alloying has been studied by transmission electron microscopy (TEM) and Mössbauer spectroscopy. The lamellar structure was found to have a range of lamellar thicknesses from about 10 nm to 200 nm. The composition and the structure of each layer were determined to be about 50 at.% iron and 50 at.% copper and FCC structure, respectively. The crystallite size in the as-milled FCC-Fe$_{50}$Cu$_{50}$ alloy varied from a few nm to a few tens of nm. From Mössbauer measurement it was found that the Fe and Cu atoms can occupy any site and the lattice can be considered as FCC with a 'random' atom at each lattice point. Nearest-neighbour atomic configuration follows that given by the binomial distribution. The driving force for the alloy formation of the system with a positive heat of mixing can be provided by the energy stored in the grain boundaries and by the configuration entropy of randomly distributed atoms in the solid solution.

Recently, a great deal of attention has been focused on the mechanical alloying mechanism by which a solid solution with a positive heat of mixing is formed upon milling [1–6]. Basically four approaches have been published to our knowledge so far. First, Veltl *et al* [1] suggested that the energy stored in the grain boundaries serves as a driving force for the formation of a solid solution. Secondly, Yavari *et al* [3] proposed that fragments with small tip radii are formed upon milling such that the capillary pressure forces the atoms at the tips of the fragments to dissolve. Eckert *et al* [4] suggested a third mechanism, which explains alloy formation by an enhanced solubility due to the high dislocation density during the initial stages of milling of the nanocrystalline powders. Very recently, Bormann and co-workers [5] proposed that the formation of a homogeneous solid solution is energetically favoured if the particle size is reduced below a critical value, which is estimated to be about 1–2 nm. The driving force is provided by the chemical contribution of the interface enthalpy and by the configuration entropy in the solid solution. In the four models the key parameter is the size of particles in the solid solution, which is mainly determined by analysis of the x-ray diffraction pattern. However, it has been suggested that the crystallite size as determined by analysis of the x-ray diffraction pattern is not a good approximation for the size of the particle in the solid solution [5]. In this letter, the microstructure of the FCC-Fe$_{50}$Cu$_{50}$ alloy was studied by transmission electron microscopy (TEM) and Mössbauer spectroscopy. The crystallite size has been estimated to be in the range of a few nm to a few tens of nm in the FCC-Fe$_{50}$Cu$_{50}$ alloy. The atomic structure of the alloy was found to be such that Fe and Cu atoms can occupy any site and the lattice can be considered as FCC with a 'random' atom at each lattice point.

For the preparation of Fe–Cu alloys, powders of iron (99.9%) and copper (99.9%) with particle sizes smaller than 100 μm were mixed to a nominal composition of 50 at.% iron and sealed in a vial in an argon atmosphere (see [6] for details). A milling time of 100 h reached the final stage. The sample consists of pellets of about 0.7 mm in diameter and about 0.3 mm in thickness. The compositions in the sample were determined by using scanning electron microscopy (SEM) with an energy dispersive x-ray analysis (EDX) facility. Values of about 0.9 at.% additional Fe and 0.35 at.% Cr originating from the abrasion of the vials and balls, could be determined. The FCC structure of the specimen was observed by x-ray diffraction measurement. TEM measurements of the specimen were performed with a Jeol 2000FX TEM operated at 200 kV equipped with an EDX facility. TEM measurements on the specimen are carried out in two ways: one with a top view and the other with a cross-sectional view. For the cross-sectional view, pellets were put in face up, sequentially, into a slotted 2 mm diameter rod. Once the rod with the samples had been fitted into a tube, an epoxy mixed with SiC was placed on top of the standing tube and then heated on the hot plate at 400 K for about 20 min. After the glue was cured, discs with thickness 0.5 mm were cut from the tube using a diamond saw and then ground to about 100 μm thickness. By further mechanical polishing the thickness of the specimen was reduced to 30 μm. Finally, a Gatan dual ion beam was used to thin the sample to electron transparency; in this procedure the specimen was cooled with liquid nitrogen.

In view of the thickness of the sample, Mössbauer spectroscopy measurements were performed in a backscattering geometry, by conversion x-ray Mössbauer spectroscopy. The conversion x-rays originating from the ^{57}Fe transition have an escape depth of about 10 μm [7]. The single line source consisted of 25 mCi ^{57}Co in a Rh matrix. All isomer shift values are given relative to the centre of α-Fe at room temperature.

Figure 1 shows top-view TEM micrographs of the as-milled FCC-Fe$_{50}$Cu$_{50}$ alloy. From figures 1(a) and 1(b), the structure was found to be fine and homogeneous with a distribution of crystallite size in a range of a few nm to a few tens of nm. A large-magnitude top-view TEM pattern is shown in figure 1(c). It is clear that there are many Moiré patterns due to crystal overlap. By calculating the spaces in four Moiré patterns, it was found that these Moiré patterns were formed by overlap of two twisted crystals with the same lattice constant.

It is well known that at an early stage of milling the lamellar microstructure was often formed in mechanically alloyed powders consisting of ductile components [8]. Each layer has a pure element composition. To date, no TEM result on the microstructure of the cross-section for the Fe–Cu system at the final stage of the milling process has been reported. Figure 2 shows TEM micrographs on the cross-section of the as-milled FCC-Fe$_{50}$Cu$_{50}$ pellet. It is very interesting that the lamellar microstructure is also formed with lamellar thickness varying from about 10 nm to 200 nm (figure 2(a)); this was not found in the top-view TEM measurements on the same sample. The composition in each layer was found by EDX to be about 50 at.% iron and 50 at.% Cu and the FCC structure was found from the diffraction pattern. This means that each layer is composed of FCC-FeCu alloy, which is completely different from the pure element composition in each layer found at an early stage of the milling. To achieve a better understanding of the microstructure of each layer in the sample, a TEM micrograph with a high magnification was obtained (figure 2(b)). The fine Moiré patterns can be clearly seen in layers. From the sizes of the Moiré patterns the crystallite size can be estimated as lying in a range from a few nm to a few tens of nm, which is in good agreement with the result found from the top-view TEM measurements. Furthermore, it can also be seen in figure 2(b) that there are many black spots in the layers. This can be explained as the precipitation of iron particles from the FCC-FeCu matrix due to heating
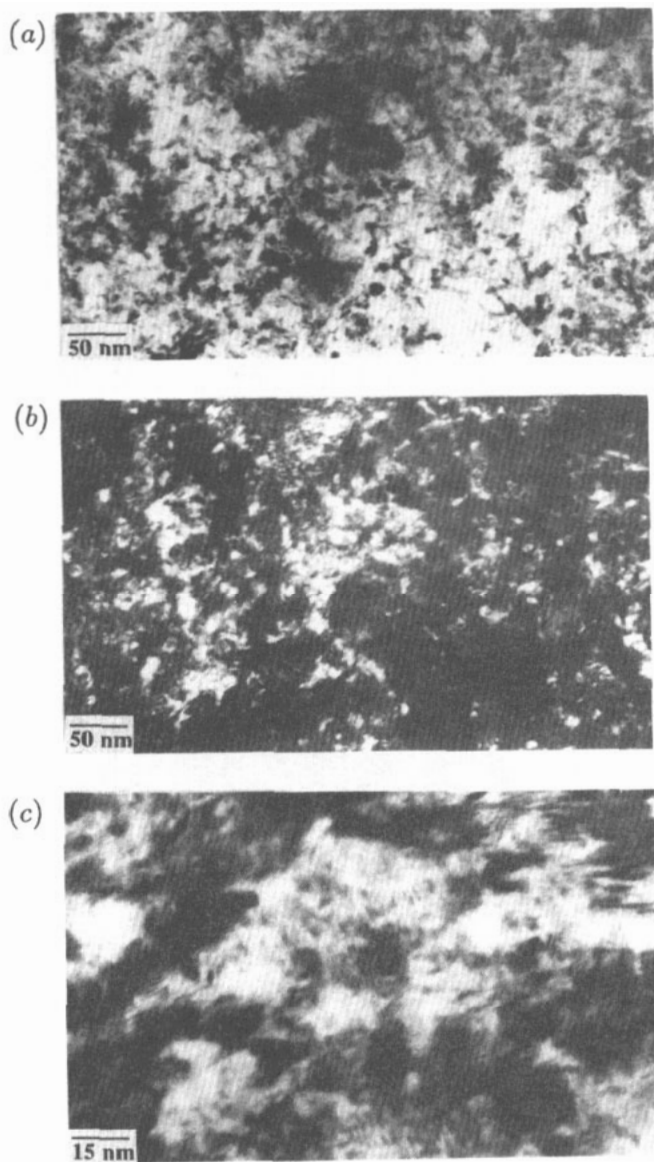
Figure 1. Top-view TEM micrographs of the FCC-Fe$_{50}$Cu$_{50}$ pellet after ball milling for 100 h; (*a*) is bright-field image, (*b*) is dark-field image, (*c*) is bright-field image with a lar magnification.

in the TEM sample preparation; this has also been found in an annealing treatment for the same sample [9]. The size of the iron particles varied from about 1 nm to 10 nm.

Figure 3 shows a Mössbauer spectrum fitted as a superposition of nine subspectra for the as-milled FCC-Fe$_{50}$Cu$_{50}$ sample. The Mössbauer parameters and the atomic configurations are listed in table 1. The eighth and ninth spectra are attributed to the residual BCC-Fe and FCC-Fe phases, respectively. The seven remaining spectra are attributed to the FCC-Fe$_{50}$Cu$_{50}$ phase. It is clear from the broad linewidths that the spectrum represents a distribution of
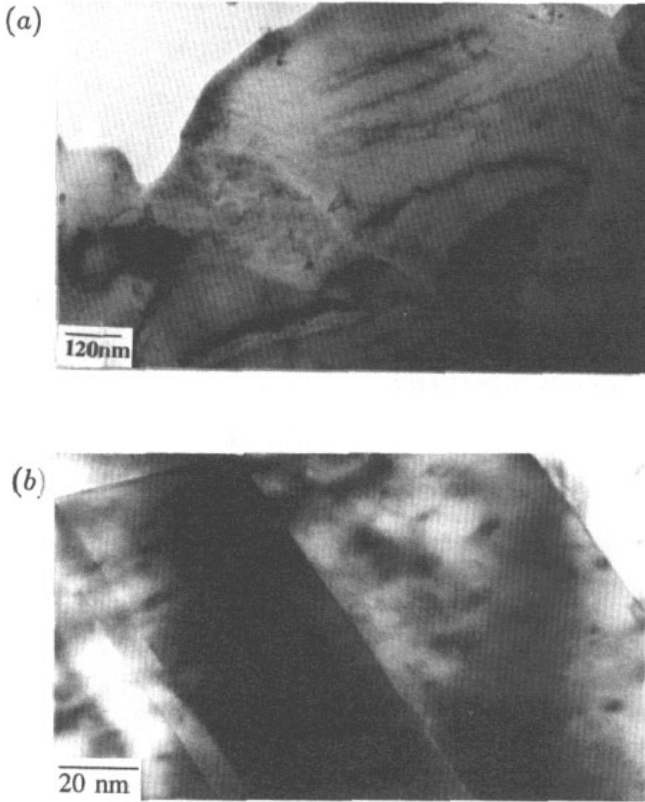
Figure 2. Cross-sectional-view TEM micrographs of the FCC-$Fe_{50}Cu_{50}$ pellet after ball milling for 100 h; (a) is bright-field image with a small magnification and (b) is bright-field image with a large magnification.

hyperfine fields. The hyperfine field can be analysed in terms of differing environments of the iron atoms arising from near-neighbour interactions. Since interactions influencing the hyperfine field are of a rather short-range character, it is valid to consider only the nearest-neighbour interactions in the FCC structure [10]. From the fitting it was found that the distribution of nearest-neighbour configurations in the FCC-FeCu phase follows the binomial distribution equation

$$P(n\text{Fe}, (12-n)\text{Cu}) = \frac{12!}{n!(12-n)!} X^n (1-X)^{12-n}$$

where $P(n\text{Fe}, (12-n)\text{Cu})$ is the probability of finding n Fe atoms and $12-n$ Cu atoms as nearest neighbours to the iron site. It is well known that the random solid solution of the FCC binary substitutional alloy has nearest-neighbour configurations following the binomial distribution. Therefore, the FCC-$Fe_{50}Cu_{50}$ alloy can be considered as a random solid solution. This result is supported by recent magnetic measurements [11]. For the fitting process two points should be noted. (1) For the FCC-$Fe_{50}Cu_{50}$ phase, the total probability of the configurations (0Fe, 12Cu), (1Fe, 11Cu), (2Fe, 10Cu), (10Fe, 2Cu), (11Fe, 1Cu) and (12Fe, 0Cu) is less than 4%, so only the other seven configurations are taken into account

in quantitative analysis of the Mössbauer spectrum; these are (3Fe, 9Cu), (4Fe, 8Cu), (5Fe, 7Cu), (6Fe, 6Cu), (7Fe, 5Cu), (8Fe, 4Cu), and (9Fe, 3Cu). (2) In the FCC-FeCu system, it is well known that those iron atoms with zero or twelve nearest-neighbour copper atoms have zero hyperfine field values at room temperature [12–14]. Therefore, it may be reasonable to assume that those iron atoms with six nearest-neighbour copper atoms will have the largest hyperfine fields. Those iron atoms with higher (7–9) or lower (5–3) Cu coordination would be expected to have reduced hyperfine field values.
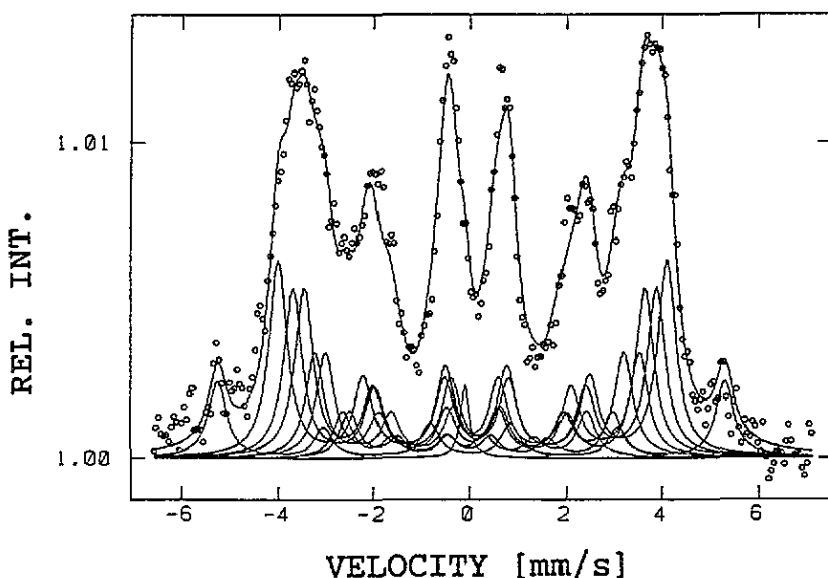

Figure 3. The Mössbauer spectrum for the unstable FCC-Fe$_{50}$Cu$_{50}$ phase fitted as a superposition of nine subspectra.

Table 1. The isomer shift (IS), hyperfine field (H), atomic configuration, relative resonance area (A), calculated $P(n\text{Fe}, (12 - n)\text{Cu})$ value and difference in hyperfine field obtained by fitting the Mössbauer spectrum for the unstable FCC-Fe$_{50}$Cu$_{50}$ phase.

No	IS (mm s^{-1})	H (kOe)	Atomic configuration	A (%)	$P(n\text{Fe}, (12 - n)\text{Cu})$ (%)	$\Delta H = H_n - H_1$ (kOe)
1	0.100 ± 0.006	251 ± 2	(6Fe, 6Cu)	20.3 ± 1.5	22.6	0
2	0.162 ± 0.011	235 ± 2	(7Fe, 5Cu)†	17.4 ± 1.3	19.3	16
3	0.074 ± 0.005	220 ± 2	(5Fe, 7Cu)	17.4 ± 1.3	19.3	31
4	0.110 ± 0.009	209 ± 2	(8Fe, 4Cu)	10.9 ± 1.3	12.1	42
5	0.131 ± 0.012	192 ± 2	(4Fe, 8Cu)	10.9 ± 1.3	12.1	59
6	0.088 ± 0.005	174 ± 2	(9Fe, 3Cu)	4.8 ± 0.6	5.4	77
7	-0.053 ± 0.005	153 ± 2	(3Fe, 9Cu)	4.8 ± 0.6	5.4	98
8	0.027 ± 0.005	328 ± 2	—	7.9 ± 0.9	—	—
9	-0.091 ± 0.005	0	—	5.7 ± 0.5	—	—

† The hyperfine field of iron atoms for the configuration (7Fe, 5Cu) is assumed to be larger than that for the configuration (5Fe, 7Cu).

According to the analyses above, we can conclude that the FCC-Fe$_{50}$Cu$_{50}$ phase prepared by mechanical alloying is a random solid solution. In this phase Fe and Cu atoms can occupy

any lattice site, the nearest-neighbour configuration following that given by the binomial distribution. From the TEM measurements the crystallite size in the FCC-$Fe_{50}Cu_{50}$ alloy was found to be in the range of a few nm to a few tens of nm. We strongly support the models proposed in [1] and [5], which suggested that the driving force for the alloy formation in the system with a positive heat of mixing can be provided by the energy stored in the grain boundaries and by the configuration entropy of the randomly distributed atoms in the solid solution.

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